

Effect of Organoclay on the Thermal Stability, Mechanical Strength, and Surface Wettability of Injection-Molded ABS–Clay Nanocomposite Materials Prepared by Melt Intercalation

Jui-Ming Yeh,¹ Chi-Lun Chen,¹ Chao-Chen Huang,¹ Fang-Chia Chang,¹ Shia-Chung Chen,² Pao-Lin Su,² Chih-Che Kuo,³ Jui-Ting Hsu,³ Boyang Chen,³ Yuan-Hsiang Yu⁴

¹Department of Chemistry and Center for Nanotechnology at CYCU, Chung-Yuan Christian University, Chung Li 32023, Taiwan, Republic of China

²Department of Mechanical Engineering, Chung-Yuan Christian University, Chung Li 32023, Taiwan, Republic of China

³TECO Nanotech Co., Ltd., 1560 Chung Shan Road, Sec. 1, Kuang-In, Taoyuan Hsien, Taiwan 320, Republic of China

⁴Department of Electronic Engineering, Lan-Yan Institute of Technology, I-Lan 261, Taiwan, Republic of China

Received 1 March 2005; accepted 24 May 2005

DOI 10.1002/app.22329

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, a series of polymer–clay nanocomposite (PCN) materials consisted of commercial thermoplastic ABS matrix and dispersing inorganic organoclay platelets were successfully prepared by melt intercalation through the twin-roller mixer. The as-prepared materials in the form of pellet were then shaped by injection-molding machine and the as-molded specimens were subsequently examined by chemical characterizations, through Fourier transformation infrared (FTIR) spectroscopy, powder X-ray diffraction (XRD), and transmission electron microscopy

(TEM). Effect of the organoclay on thermal stability, mechanical strength, and surface wettability of PCN materials, in both the form of standard dumbbell shape and pellet, was studied using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), tensile test, hardness test, and contact-angle measurements, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1576–1582, 2006

Key words: ABS; clay; nanocomposite; melt intercalation

INTRODUCTION

Lately, layered materials, such as smectite clays (e.g., montmorillonite, MMT) have attracted intense research interests for the preparation of polymer–clay nanocomposite (PCN) materials. PCN materials usually exhibit unique properties superior to traditional composites and conventional materials. Generally, they combine both the characteristics of the inorganic material and the organic polymer. PCN material is a promising system because the clay possess a high aspect ratio and a platy morphology and can be employed to boost the physical properties (e.g., thermal stability,¹ mechanical strength,² fire retardant,³ gas barrier,⁴ and corrosion protection^{5–16}) of bulk polymers.

Four common approaches are generally used to prepare PCN materials: exfoliation–adsorption, in situ polymerization, melt intercalation, and template syn-

thesis.¹⁷ Among these approaches, melt intercalation is an efficient method to synthesize PCN materials and has been exhibited to be a more powerful and environmentally-benign alternative to other approaches. The melt intercalation method is remarkable because it can produce both intercalated and exfoliated composites with a wide range of polymers from nonpolar polymers (e.g., polystyrene,^{18,19} polyethylene,²⁰ polypropylene²¹) to weakly polar polymers [e.g., poly(ethylene terephthalate),¹⁸ poly(methyl methacrylate)²²] to strongly polar nylon.²³

Acrylonitrile–butadiene–styrene (ABS) is a popular engineering thermoplastic because of its unique properties, including excellent mechanical properties, chemical resistance, and processing abilities. However, few reports associated with the ABS–clay nanocomposite materials have been published. For example, Lee et al. reported the synthesis of ABS–montmorillonite (MMT) nanocomposites by emulsion polymerization.²⁴ Hu et al. reported the preparation and thermal properties of ABS–montmorillonite nanocomposite.^{25–29} In this paper, we study the effect of organoclay on thermal stability, mechanical strength, and surface wettability of injection-molded ABS–clay nanocomposite materials, in both the form of standard

Correspondence to: J.-M. Yeh (juiming@cycu.edu.tw).

Contract grant sponsor: NSC; contract grant number: 92-2113M-033-011.

dumbbell shape and pellet, based on the studies of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), tensile test, hardness test, and contact-angle measurements, respectively.

EXPERIMENTAL

Chemicals and instrumentations

Commercial ABS (PA-717 C) was purchased as pellets from Qimei Stock Company, Taiwan. Hexadecyltrimethyl ammonium bromide (Sigma), melamine (Lancaster), *n*-decyltrimethylammonium chloride (TCI), 1,4-phenylenediamine (Lancaster), *n*-decyltrimethylammonium bromide (Lancaster), dodecyltrimethylammonium chloride (Fluka), octyltrimethylammonium bromide (Fluka), 4,4'-azodianiline (Acros), and dodecylamine (Fluka) were used as-received without further purification. The montmorillonite clay (PK805), purchased from Pai-Kong Ceramic Company (Taiwan), was used, and had a CEC value of 98 meq/100 g.

FTIR spectra were measured on pressed KBr pellets, using a JASCO FT/IR-460 plus spectrometer. Wide-angle X-ray diffraction study of the samples was performed on a Rigaku D/MAX-3C OD-2988N X-ray diffractometer with a copper target and Ni filter at a scanning rate of 4°/min. The samples for transmission electron microscopy (TEM) study was first prepared by putting the membrane of PCN materials into epoxy resin capsules followed by curing the epoxy resin at 100°C for 24 h in a vacuum oven. Then the cured epoxy resin containing PCN materials were microtomed with a Reichert-Jung Ultracut-E into 60–90-nm thick slices. Subsequently, one layer of carbon about 10-nm thick was deposited on these silices on mesh 100 copper nets for TEM observations on a JEOL-200FX, with an acceleration voltage of 120 kV. Centrifugal Ball Mill (Retsch S100) was used to mill the size of organophilic clay smaller than 8 mm. Twin-roll mill (Kobelco, model KXY-30) was used to melt-mix the organoclay and ABS. Injection molding machine manufactured by Practical Machine Company (Taiwan, model no. VS-100) was used to make the as-prepared sample in the form of standard dumbbell shape.

A DuPont thermal analysis system equipped with model TA Q10 DSC and TA Q50 TGA was used for the thermal analyses under N₂ and air flow. The programmed heating rate was 10°C/min. The tensile test of PCN membranes was carried out through a tensile test analyzer manufactured by Hong-Da Company (Taiwan, with model no. HT-8503). Hardness tests were run on a TECLOCK microhardness tester with Type D (model GS-720N) and Type A (model GS-706N) for high and low hardness samples, respectively, and an indentation time of 10 s at 25°C. The

contact angle of water was measured with a contact-angle meter with a model FTA25 (First Ten Angstroms).

Preparation of organoclay

The organoclay was prepared by a cationic-exchange reaction between the sodium cations of MMT clay and quaternary alkylphosphonium cations of intercalating agent. The equation for calculating the intercalating agent used for cationic-exchange reaction was as follows:

$$98/100 \times 5 \text{ g (for clay)} \times 1.2 \\ = (X/M_w \text{ of intercalating agent}) \times 1 \times 1000$$

where X represented the amount of used intercalating agent, 98/100 represent the CEC value per 100 g of MMT clay, 1.2 (>1) indicating the excess amount of intercalating agent was used. Typically, 30 g of MMT clay with a CEC value of 98 meq/100 g was stirred overnight in 1000-mL distilled water (beaker A) at room temperature. A separate solution containing excess amount of intercalating agent (12.8 g) in another 200 mL of distilled water (beaker B) was stirred for 1 h using a magnetic stirrer, followed by adding 1M HCl aqueous solution to adjust the pH value to about 3–4. After stirring for 1 h, the protonated amino acid solution (beaker B) was added at a rate of approximately 10 mL/min, with vigorous stirring, to the MMT suspension (beaker A). The mixture was stirred overnight at room temperature. The organoclay was recovered by filtering the solution in a Buchner funnel. Purification of products was performed by washing and filtering the samples repeatedly for at least three times to remove any excess of ammonium ions.

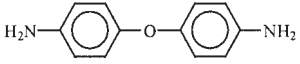
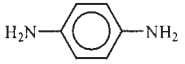
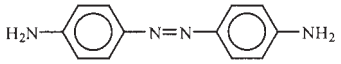
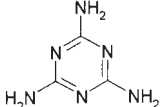
Preparation of ABS–clay nanocomposite materials through melt intercalation

The as-prepared organoclay was first milled by centrifugal Ball Mill machine (S-100) and followed by melt-mixing at 200°C by using a twin-roll mill for ~15 min under vacuum. The melt-mixing procedure of ABS–clay composites was performed twice to gain products in the form of pellet with better blending. The as-prepared ABS–clay nanocomposite pellets were subsequently injection-molded by a injection molding machine to obtain nanocomposites with standard dumbbell-shaped specimens for the following investigations.

RESULTS AND DISCUSSION

In this study, 10 intercalating agents were used for the cationic-exchange reaction with the Na⁺ and Ca²⁺

TABLE I
Summary of XRD Data Obtained from Organoclay-Modified by Different Intercalating Agents

Compound code	2θ	d -Spacing (Å)
Na ⁺ -MMT (PK-805)	6.80	12.91
 4,4'-Oxydianiline	6.00	14.72
 1,4-Phenylenediamine	5.66	15.60
 4,4'-Azodianiline	6.60	13.38
Dodecylamine (CH ₃ (CH ₂) ₁₁ NH ₃ ⁺ Br ⁻)	4.80	18.39
Octyltrimethyl ammonium bromide (CH ₃ (CH ₂) ₁₀ NH ₃ ⁺ Br ⁻)	6.25	14.13
Dodecyltrimethyl ammonium chloride (CH ₃ (CH ₂) ₁₄ NH ₃ ⁺ Cl ⁻)	4.75	18.59
<i>n</i> -Decyltrimethyl ammonium chloride (CH ₃ (CH ₂) ₉ N(CH ₃) ₃ ⁺ Cl ⁻)	5.10	17.31
<i>n</i> -Decyltrimethyl ammonium bromide (CH ₃ (CH ₂) ₉ N(CH ₃) ₃ ⁺ Br ⁻)	5.20	16.98
 Melamine	6.90	12.80
Hexadecyltrimethyl ammonium bromide (C ₁₉ H ₄₂ NBr)	4.40	20.06

residing in the interlayer regions of montmorillonite clay. The values of 2θ and their corresponding d -spacing of each used intercalating agent, based on the measurements of powder X-ray diffraction (XRD) patterns were shown in Table I. Among other intercalating agent used, hexadecyltrimethylammonium bromide-modified organoclay was found to display a highest value of d -spacing at ~ 20 Å, and therefore was chosen to be used in the subsequent studies associated with the melt intercalation of polymers. The composition of the ABS-clay nanocomposite materials was varied from 0 to 5 wt % of organoclay with respect to the ABS content as summarized in Table II.

Characterization

The representative FTIR spectra of the organoclay, bulk ABS, and PCN materials were shown in Figure 1.

The characteristic vibration bands of ABS were at 763 and 698 cm⁻¹ (aromatic), 1670 cm⁻¹ (C=C), and 2238 cm⁻¹ (C-N), and those of organoclay were shown at 1040 cm⁻¹ (Si-O), 523 cm⁻¹ (Al-O), and 464 cm⁻¹ (Mg-O).⁵ As the loading of organoclay was increased, the intensities of organoclay bands become stronger in the FTIR spectra of PCN materials. Figure 2 showed the wide-angle powder XRD patterns of raw clay (Na⁺-montmorillonite), organoclay, and a series of PCN materials. For CLABS1, there is a lack of any diffraction peak in $2\theta = 2$ –10°, as opposed to the diffraction peak at $2\theta = 4.40^\circ$ (d -spacing = 20.06 Å) for organoclay, indicating the possibility of having exfoliated silicate nanolayers of organoclay dispersed in the ABS matrix. When the amount of organoclay increased to 5 wt %, there is a small peak appearing at $2\theta = 2.80^\circ$, corresponding to a d -spacing of 31.53 Å. This implied that there was a small amount of organoclay

TABLE II
Relations of Composition of ABS-Clay Nanocomposite Materials Prepared by Melt Intercalation, with Thermal Stability, Mechanical Strength, and Contact Angle

Compound Code	Feed Composition		Thermal Properties (°C)		Tensile Strength (kg/mm ²)	Elongation (%)	Hardness (mN)	Contact Angle (degree)
	ABS	MMT	T _d ^a	T _g ^b				
ABS	100	0	374.9	97.3	3.9	11	63	78
CLABS1	99	1	377.9	103.1	4.1	5	70	82
CLABS3	97	3	378.2	104.5	4.5	4.5	75	83
CLABS5	95	5	381.6	106.2	3.7	4	78	83.5

^a As determined by TGA, at 10 wt% weight loss.

^b As determined by DSC.

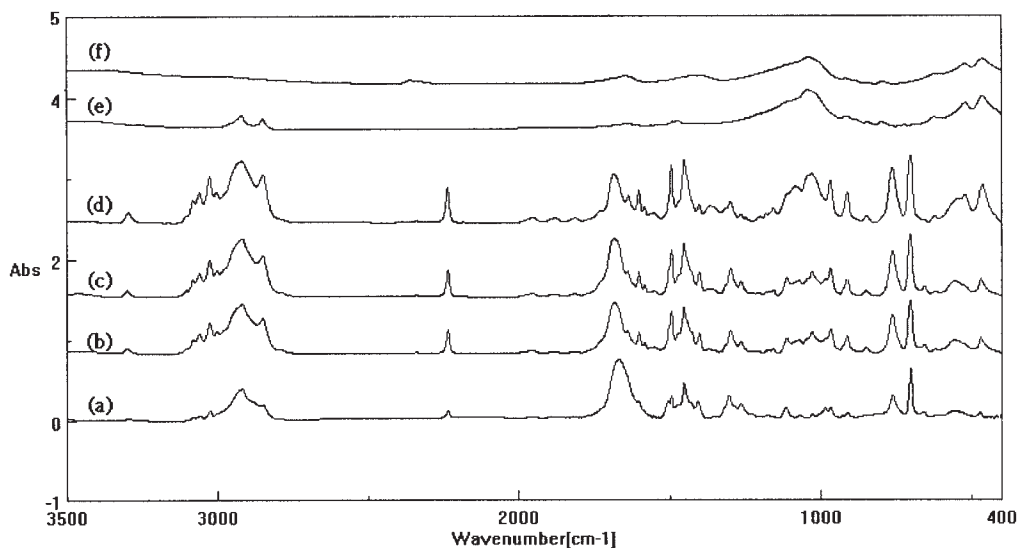


Figure 1 The representative FTIR spectra of (a) neat ABS (b) CLABS1 (c) CLABS3 (d) CLABS5 (e) organophilic clay (f) Na^+ -clay.

that cannot be exfoliated in the ABS and existed in the form of an intercalated layer structure. For the morphological image studies, as shown in Figure 3(a), TEM micrograph of CLABS3 at $50,000\times$ magnification revealed that organoclay platelets showed a dispersion of mainly exfoliated structure in the ABS matrix. Furthermore, TEM of PCN materials with 5 wt % clay loading (i.e., CLABS5) at $50,000\times$ magnification indicated that the nanocomposite displayed a mixed nanomorphology, as shown in Figure 3(b). Individual silicate layers, along with two and three layer stacks, were found to be exfoliating in the ABS matrix. In addition, some larger intercalated tactoids can also be identified.

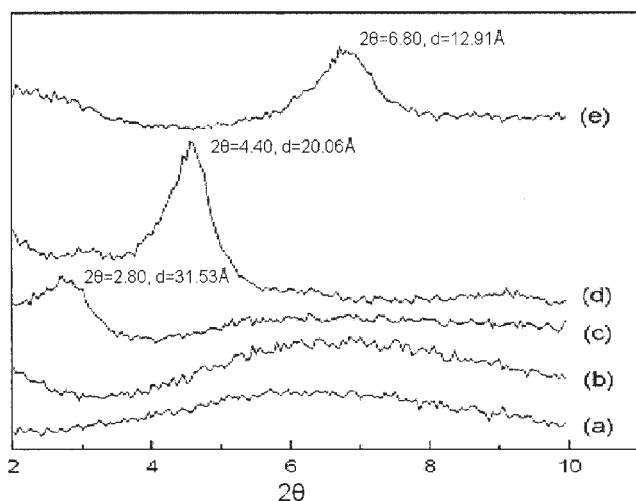


Figure 2 The powder X-ray diffraction pattern of (a) neat ABS (b) CLABS1 (c) CLABS5 (d) organophilic clay (e) Na^+ -clay.

Thermal stability

Figure 4 showed typical TGA curves of the PCN materials in the form of pellet as well as that of neat ABS, as measured under an air atmosphere. In general, there appeared one major stage of weight loss starting at $\sim 300^\circ\text{C}$ and ending at $\sim 800^\circ\text{C}$, which might be correspondent to the structural decomposition of the polymers. According to the published reports on PCN materials, the unparalleled ability of smectite clays was found to boost the thermal stability of polymers.^{1,5-16} Evidently, we found that the onset of the thermal decomposition of those PCN materials shifted slightly toward higher temperature range than that of neat ABS, which confirmed the enhancement of intercalated polymers. After $\sim 700^\circ\text{C}$, the curves are all leveled off, and mainly the inorganic residue (e.g.,

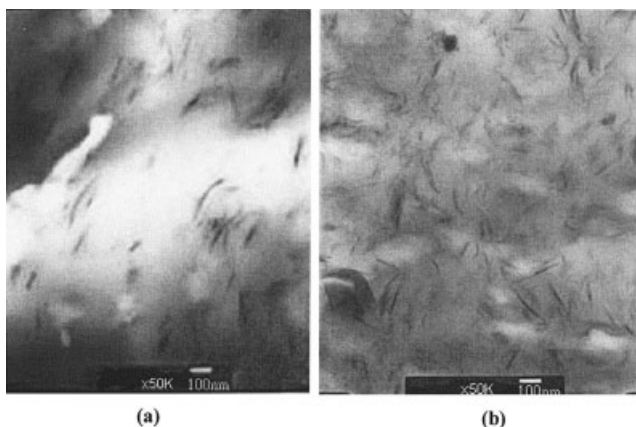


Figure 3 Transmission electron microscopy micrographs of (a) CLABS3 at $\times 50,000$ magnification (b) CLABS5 at $\times 50,000$ magnification.

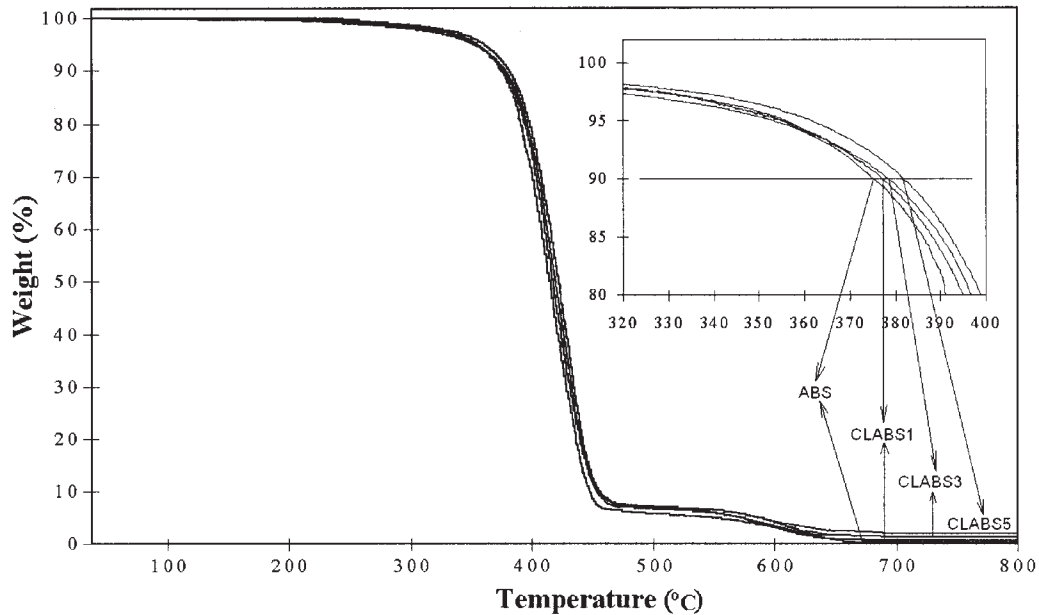


Figure 4 TGA curves of ABS and a series of ABS-clay nanocomposite materials.

Al₂O₃, MgO, SiO₂) remained. We also found from the DSC measurements that the incorporation of organoclay resulted in an increase in the T_g (heating scan) relative to neat ABS, as shown in Figure 5. This was tentatively associated with the confinement of the intercalated polymer chains within the organoclay galleries that prevent the segmental motions of the polymer chains.^{1,5-16} As the loading of organoclay platelets was increased, the T_g of PCN materials became higher.

Mechanical strength

Relationship between tensile properties and organoclay loading as obtained from tensile test on the standard dumbbell-shaped specimen of ABS-clay nano-

composite materials was studied, as shown in Figure 6. For example, we found that the incorporation of organoclay platelets into polymer matrix increased the tensile strength of ABS up to 3 wt % organoclay loading. Furthermore, excess amount of organoclay loading (e.g., 5 wt %) was found to decrease the tensile strength of as-prepared nanocomposite materials. On the other hand, elongation of the ABS-clay nanocomposite materials was decreasing as the organoclay loading increased in the composite, as shown in Figure 7. The hardness is an important parameter for evaluating or designating hybrid materials. The hardness data of the ABS-clay nanocomposite materials in the form of standard dumbbell shape at various ma-

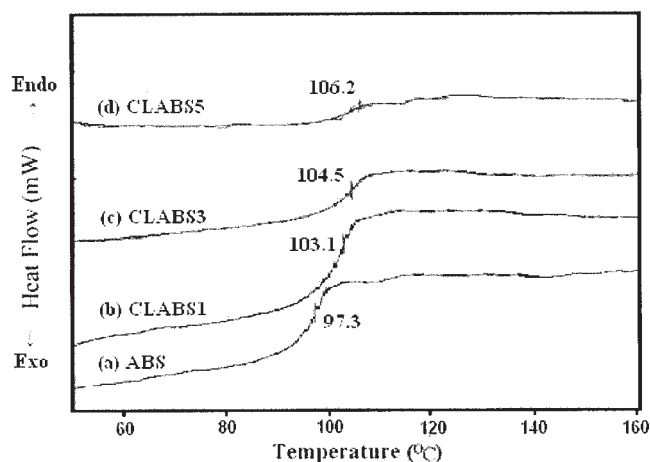


Figure 5 DSC curves of ABS and a series of ABS-clay nanocomposite materials.

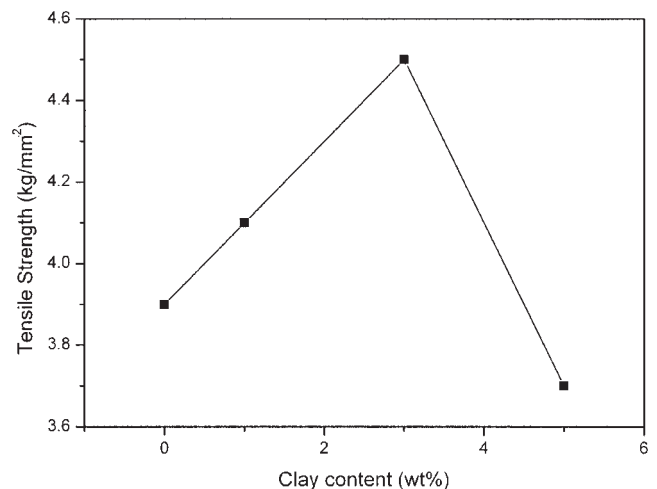


Figure 6 Tensile strength versus organoclay loadings for ABS-clay nanocomposite materials.

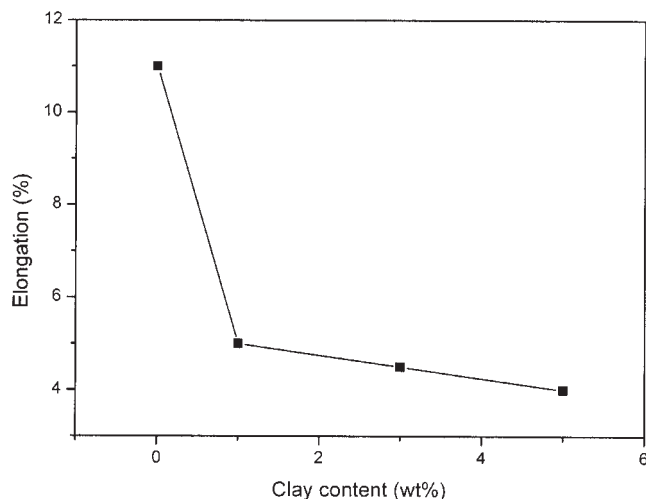


Figure 7 Elongation versus organoclay loadings for ABS-clay nanocomposite materials.

terial compositions are given in Figure 8 and Table II. The neat injection-molded ABS have relatively low hardness (i.e., 63 mN). Upon addition of organoclay into ABS, the hardness increased to 70 mN for CLABS1, to 75 mN for CLABS3, and to 78 mN for CLABS5. Thus, the hardness of the polymers can be improved significantly by the incorporation of organoclay platelets via melt intercalation approach and can be controlled by varying the organoclay content in the nanocomposite materials.

Contact-angle (wettability) measurements

The contact angle measured on First Ten Angstroms contact-angle meter (model FTA25) at 26°C, using triple-distilled water. Sets of droplets (sessile drop; vol-

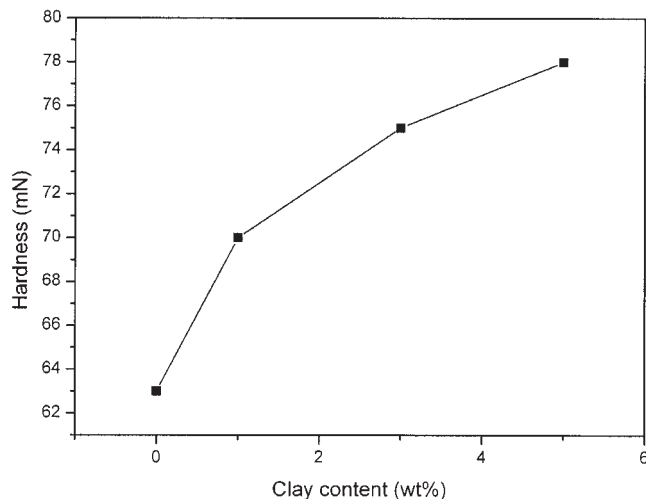


Figure 8 Hardness versus organoclay loadings for ABS-clay nanocomposite materials.

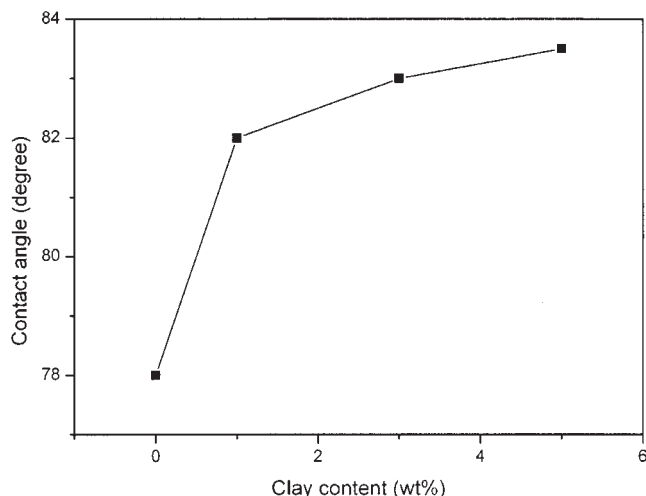


Figure 9 Contact-angle (wettability) of ABS-clay nanocomposite materials.

ume of approximately 1.0 μL) of water were placed on a surface of standard dumbbell-shaped sample. The dimensions of the droplets were measured approximately 10 s after placing the droplets. At least five parallel measurements were performed. The contact angle was calculated by the following conditions:

$$\text{Contact angle} = 2 \tan^{-1} (h/r)$$

where h was the height of the spherical segment, and r , the radial of the spherical segment. In this study, contact angle of H_2O on the ABS-clay nanocomposite materials showed that the increase of clay content resulted in the increase of contact angle, as shown in Figure 9 and Table II. For example, the neat injection-molded ABS showed low contact angle of water droplet (i.e., 78°). Upon addition of organoclay into ABS, the contact angle increased to 82° for CLABS1, to 83° for CLABS3, and to 83.5° for CLABS5. This implied that the hydrophobicity of the ABS-clay nanocomposite materials increased with an increasing organoclay content. Thus, the incorporation of organoclay platelets into the ABS matrix does indeed change the surface characteristics of the nanocomposite materials significantly.

CONCLUDING REMARKS

In this article, a series of PCN materials consisted of commercial ABS and organoclay platelets were successfully prepared through melt intercalation approach. The as-prepared PCN materials were subsequently characterization by FTIR, powder XRD, and TEM. We found that injection-molded PCN materials at low clay loading, in both the form of standard dumbbell shape and pellet, showed an enhanced ther-

mal stability and mechanical strength based on the studies of TGA, DSC, tensile test, and hardness test, respectively. Furthermore, the incorporation of organoclay platelets into ABS matrix showed an increase of hydrophobicity, based on the contact-angle measurements.

References

1. Tyan, H.-L.; Liu, Y.-C.; Wei, K.-H. *Chem Mater* 1999, 11, 1942.
2. Wang, Z.; Pinnavaia, T.-J. *Chem Mater* 1998, 10, 3769.
3. Gilman, J.-W.; Jackson, C.-L.; Morgan, A.-B.; Hayyis, R., Jr.; Manias, E.; Giannelis, E.-P.; Wuthenow, M.; Hilton, D.; Phillips, S.-H. *Chem Mater* 2000, 12, 1866.
4. Lan, T.; Kaviratna, P.-D.; Pinnavaia, T.-J. *Chem Mater* 1994, 6, 573.
5. Yeh, J.-M.; Liou, S.-J.; Lai, C.-Y.; Wu, P.-C.; Tsai, T.-Y. *Chem Mater* 2001, 13, 1131.
6. Yeh, J.-M.; Liou, S.-J.; Lin, C.-Y.; Cheng, C.-Y.; Chang, Y.-W.; Lee, K.-R. *Chem Mater* 2002, 14, 154.
7. Yeh, J.-M.; Chen, C.-L.; Chen, Y.-C.; Ma, C.-Y.; Lee, K.-R.; Wei, Y.; Li, S. *Polymer* 2002, 43, 2729.
8. Yeh, J.-M.; Chin, C.-P.; Chang, S. *J Appl Polym Sci* 2003, 88, 3264.
9. Yeh, J.-M.; Chin, C.-P. *J Appl Polym Sci* 2003, 88, 1072.
10. Yu, Y.-H.; Yeh, J.-M.; Liou, S.-J.; Chang, Y.-P. *Acta Mater* 2004, 52, 475.
11. Yu, Y.-H.; Yeh, J.-M.; Jen, C.-C.; Huang, H.-Y.; Wu, P.-C.; Huang, C.-C. *J Appl Polym Sci* 2004, 91, 3438.
12. Yeh, J.-M.; Liou, S.-J.; Lin, C.-G.; Chang, Y.-P.; Yu, Y.-H. *J Appl Polym Sci* 2004, 92, 1970.
13. Yeh, J.-M.; Liou, S.-J.; Lu, H.-J.; Huang, H.-Y. *J Appl Polym Sci* 2004, 92, 2269.
14. Yeh, J.-M.; Chen, C.-L.; Chen, Y.-C.; Ma, C.-Y.; Yu, Y.-H.; Huang, H.-Y. *J Appl Polym Sci* 2004, 92, 631.
15. Yeh, J.-M.; Chen, C.-L.; Kuo, T.-H.; Su, W.-F.; Huang, H.-Y.; Liaw, D.-J.; Lu, H.-Y.; Liu, C.-F.; Yu, Y.-H. *J Appl Polym Sci* 2004, 92, 1072.
16. Yu, Y.-H.; Yeh, J.-M.; Liou, S.-J.; Chen, C.-L.; Liaw, D.-J.; Lu, H.-Y. *J Appl Polym Sci* 2004, 92, 3573.
17. Alexandre, M.; Dubois, P. *Mater Sci Eng* 2000, 28, 63.
18. Krishnamoorti, R.; Vaia, R.-A.; Giannelis, E.-P. *Chem Mater* 1996, 8, 1728.
19. Vaia, R.-A.; Jandt, K.-D.; Kramer, E.-J.; Giannelis, E.-P. *Chem Mater* 1996, 8, 2628.
20. Wang, S.; Hu, Y.; Tang, Y.; Wang, Z.; Chen, Z.; Fan, W. *J Appl Polym Sci* 2003, 89, 2583.
21. Tang, Y.; Hu, Y.; Wang, S.; Gui, Z.; Chen, Z.; Fan, W. *J Appl Polym Sci* 2003, 89, 2586.
22. Kumar, S.; Jog, J.-P.; Natarajan, U. *J Appl Polym Sci* 2003, 89, 1186.
23. Liu, L.; Qi, Z.; Zhu, X. *J Appl Polym Sci* 1999, 71, 1133.
24. Lee, W.-J.; Chul, M.-K.; Dong, C.-L. *J Polym Sci Part B: Polym Phys* 2001, 39, 719.
25. Wang, S.; Hu, Y.; Song, L.; Wang, Z.; Chen, Z.; Fan, W. *Polym Degrad Stab* 2002, 77, 423.
26. Wang, S.; Hu, Y.; Song, L.; Wang, Z.; Chen, Z.; Fan, W. *Polym Degrad Stab* 2003, 80, 157.
27. Zong, R.; Hu, Y.; Wang, S.; Song, L. *Polym Degrad Stab* 2004, 83, 423.
28. Wang, S.; Hu, Y.; Zong, R.; Tang, Y.; Chen, Z.; Fan, W. *Appl Clay Sci* 2004, 25, 49.
29. Wang, S.; Hu, Y.; Lin, Z.; Gui, Z.; Wang, Z.; Chen, Z.; Fan, W. *Polym Int* 2003, 52, 1045.